Supporting Information

Ultra-High Activity and Broad-Spectrum Temperature Resistance of Amine-Imine Cobalt Pre-Catalysts in Butadiene Polymerization

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Table S1. Thermostability of the Co3 systems at 80°C and 100°C[a]

								microstructure[d]	
run	**Al**	**T(°C)**	**t(min)**	**yield**	**Activity[b]**	**M_n[c]/10^4**	**PDI**	***cis*-1,4**	**trans-1,4**	**1,2**
1	100	80	10	83.3%	6759	14.9	4.71	92.2%	4.6%	3.2%
2	100	80	60	87.5%	1183	33.5	4.45	90.3%	4.7%	5.0%
3	100	80	120	92.2%	623	35.2	3.68	90.5%	5.4%	4.1%
4	100	100	10	72.9%	5915	14.2	4.33	87.4%	8.5%	4.1%
5	100	100	60	84.4%	1041	15.9	4.77	88.9%	7.9%	3.2%
6	100	100	120	85.8%	580	24.1	3.99	88.3%	7.3%	4.4%

[a] Polymerization conditions: in toluene, [Bd] = 0.13 g/mL, [Bd]/[Co] = 25000, EASC as a co-catalyst. [b] Activity in units of $kg_{polymer}$·mol^{-1}·h^{-1}. [c] M_n and PDI were determined by GPC. [d] Determined by IR and ^{1}H-NMR.

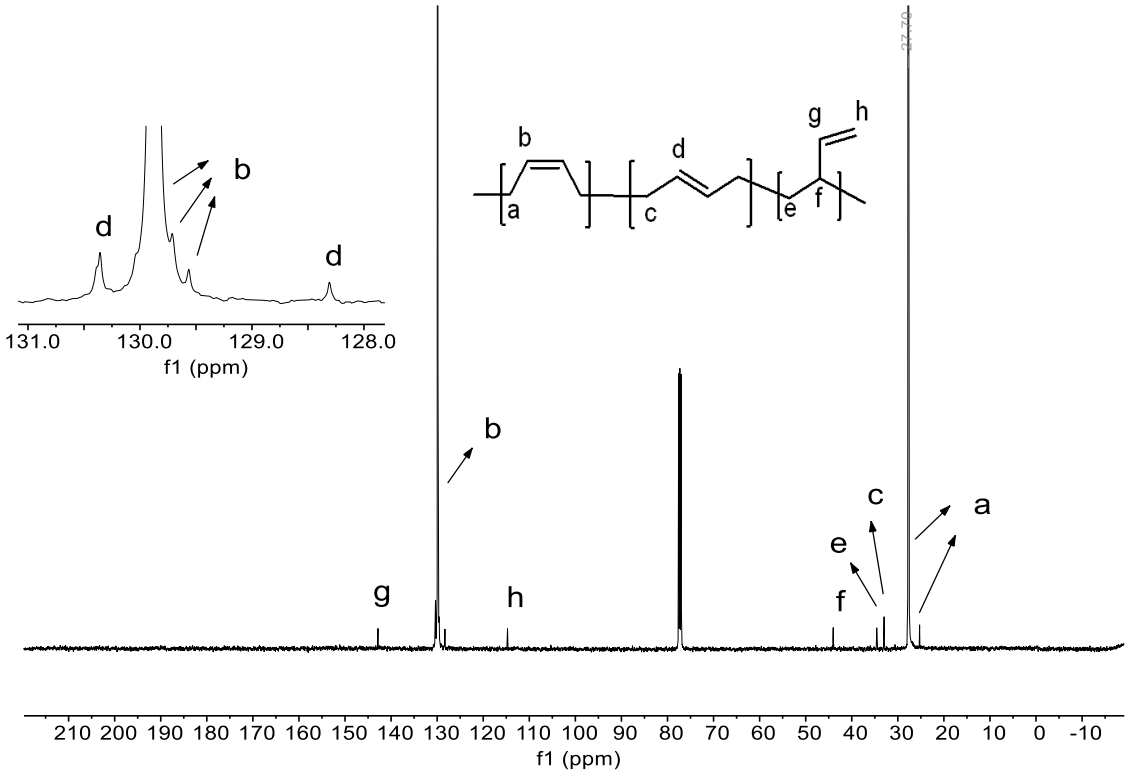

Figure S1. Representative ^{13}C NMR spectrum and its assignment[1-3] (Co3, Table 4)

1. M. A. Krajewski-Bertrand and F. Lauprêtre, *Macromolecules*, 1996, 29, 7616-7618.

2. G. Van der Velden, C. Didden, T. Veermans and J. Beulen, *Macromolecules*, 1987, 20, 1252-1256.

3. A. D. H. Clague, J. A. M. van Broekhoven and L. P. Blaauw, *Rubber Chemistry and Technology*, 1974, 47, 1136-1150.

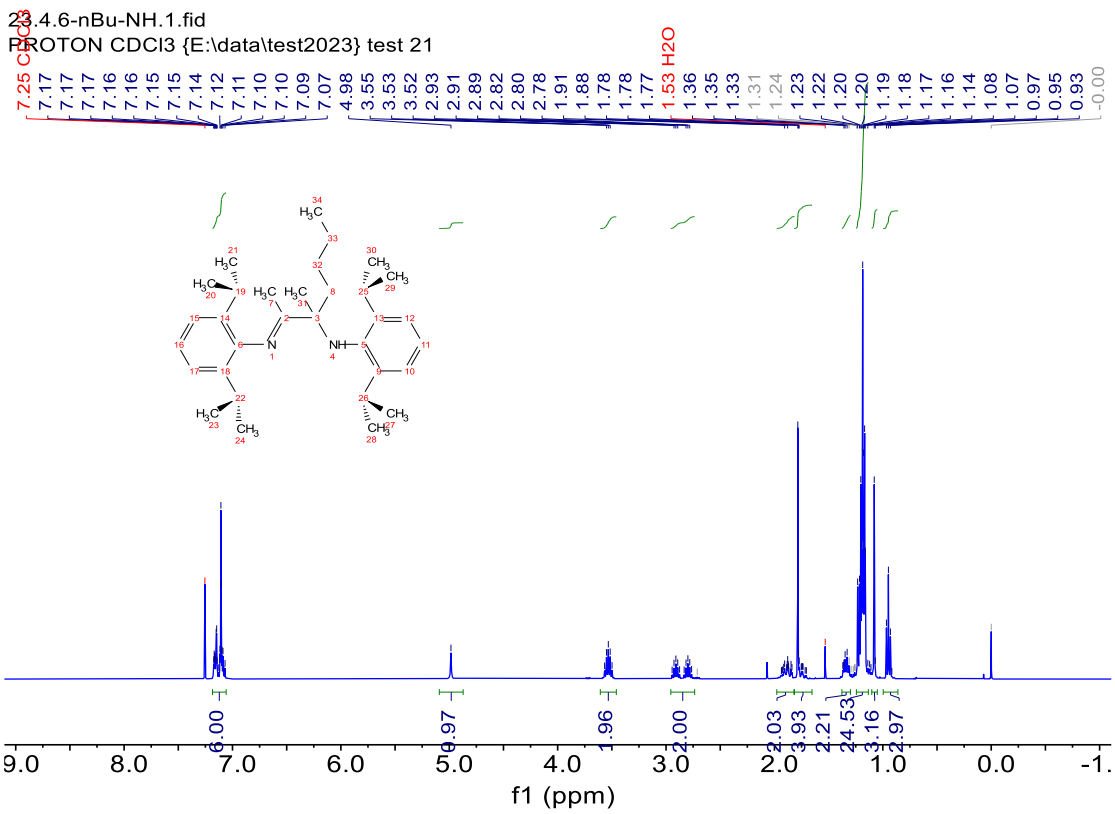

Figure S2. ^{1}H NMR spectrum of L1

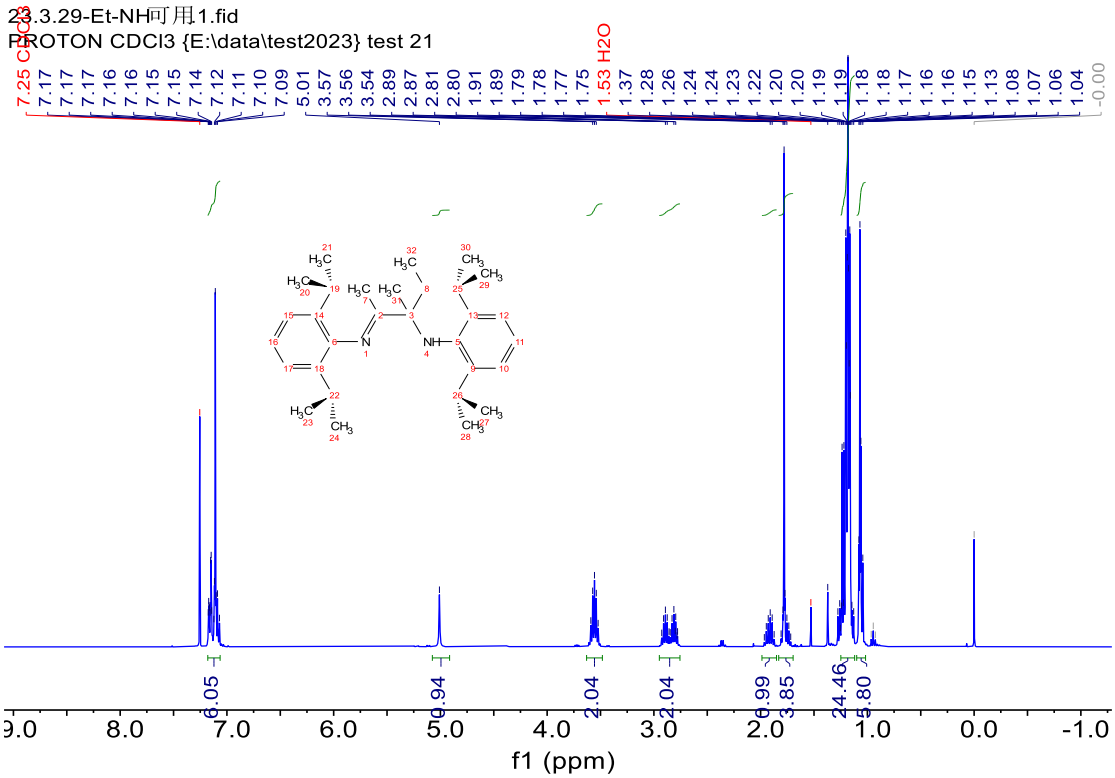

Figure S3. ^{1}H NMR spectrum of L2

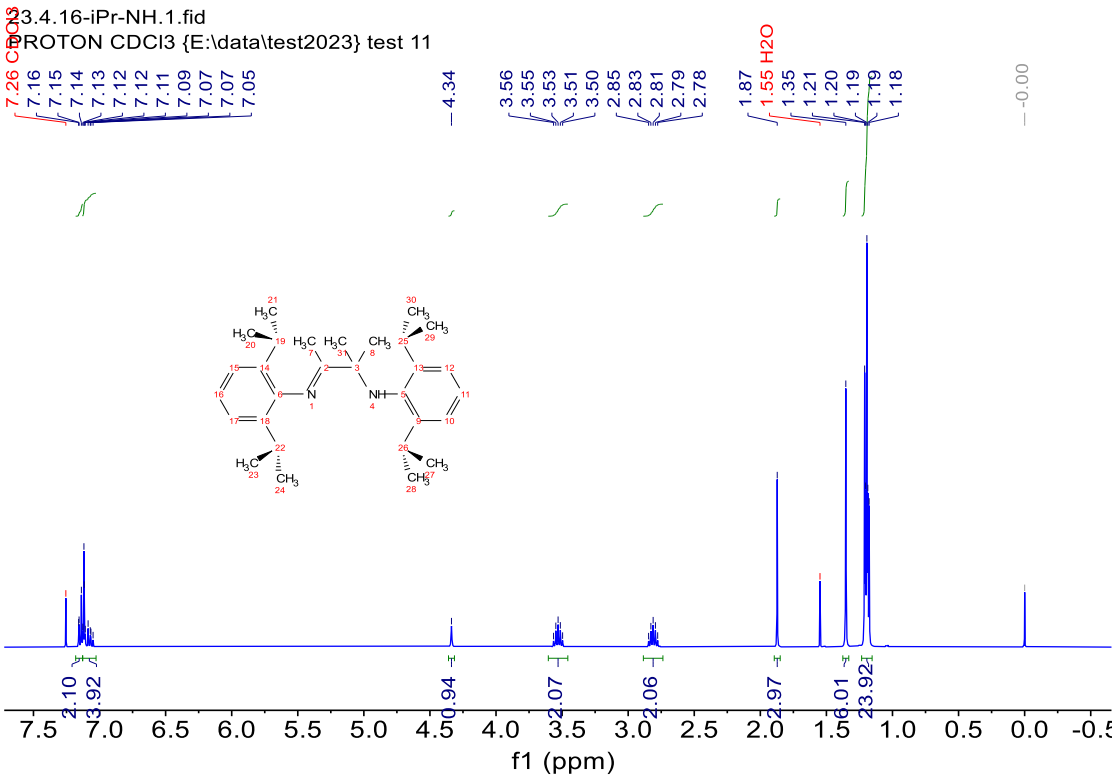

Figure S4. ^{1}H NMR spectrum of L3

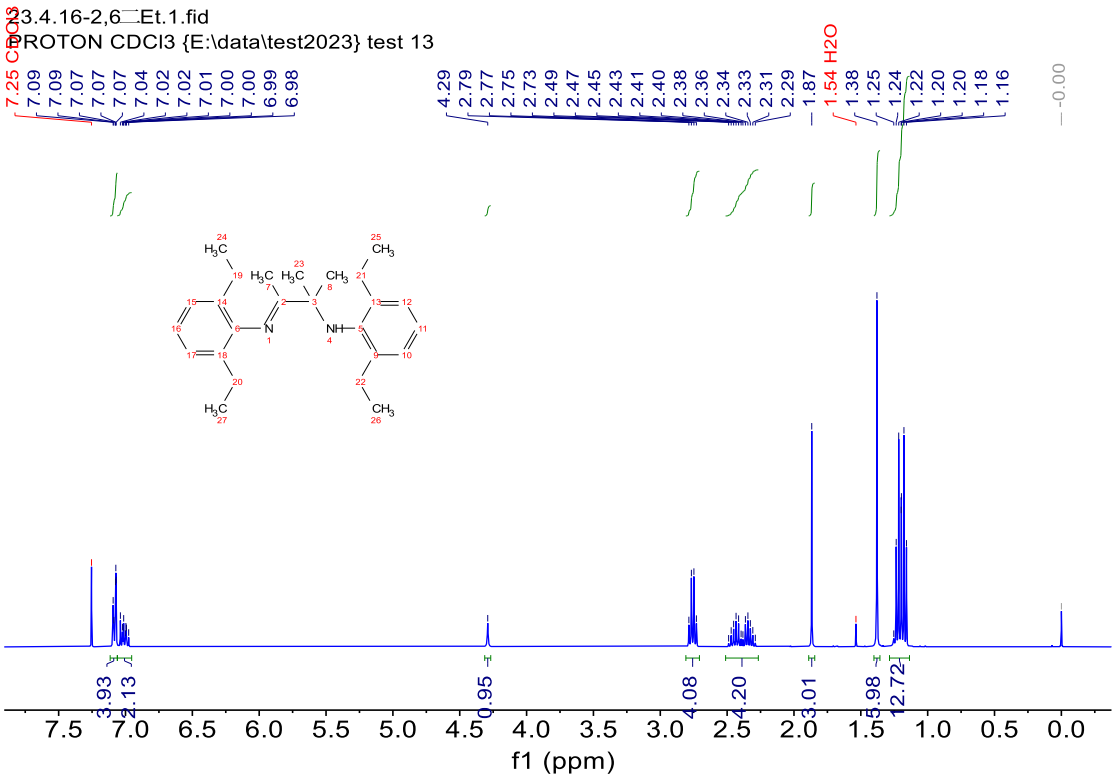

Figure S5. ^{1}H NMR spectrum of L4

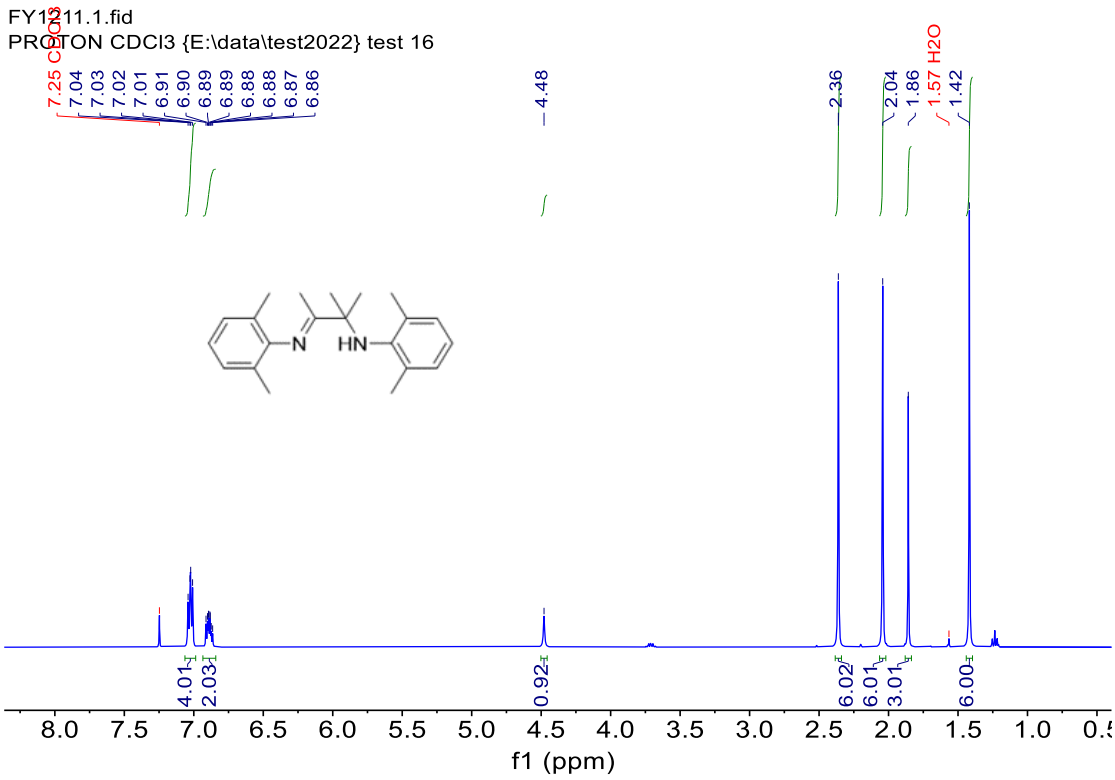

Figure S6. ^{1}H NMR spectrum of L1

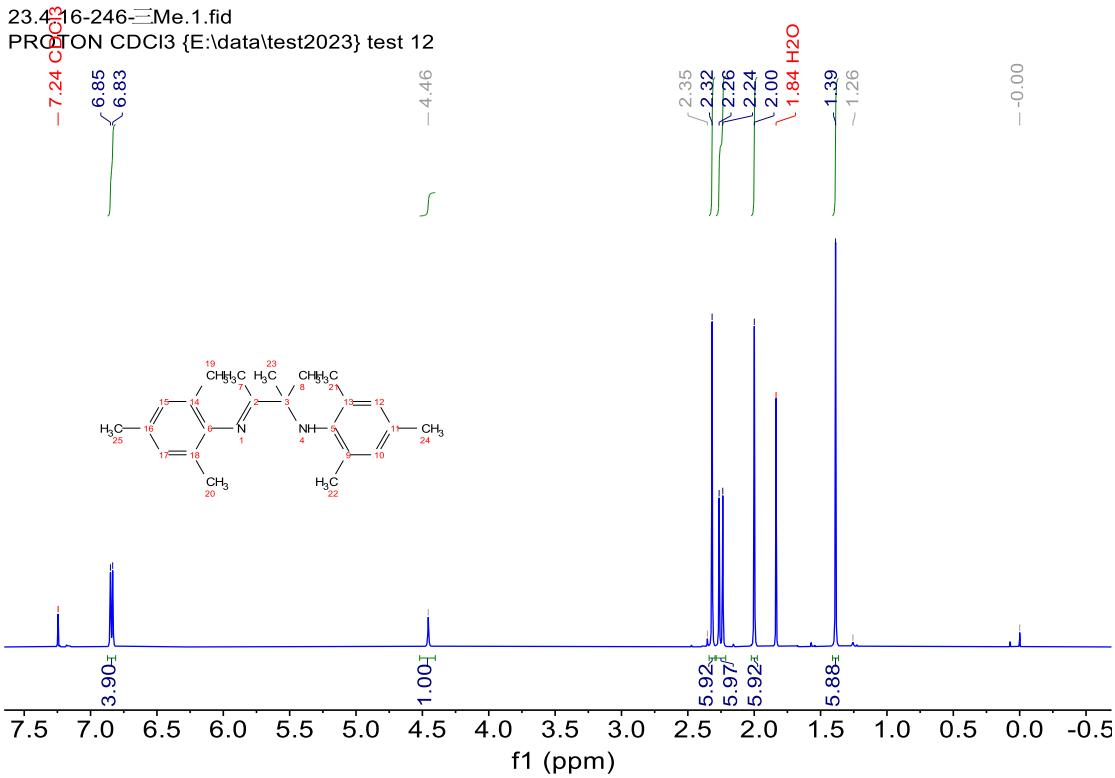

Figure S7. ^{1}H NMR spectrum of L6

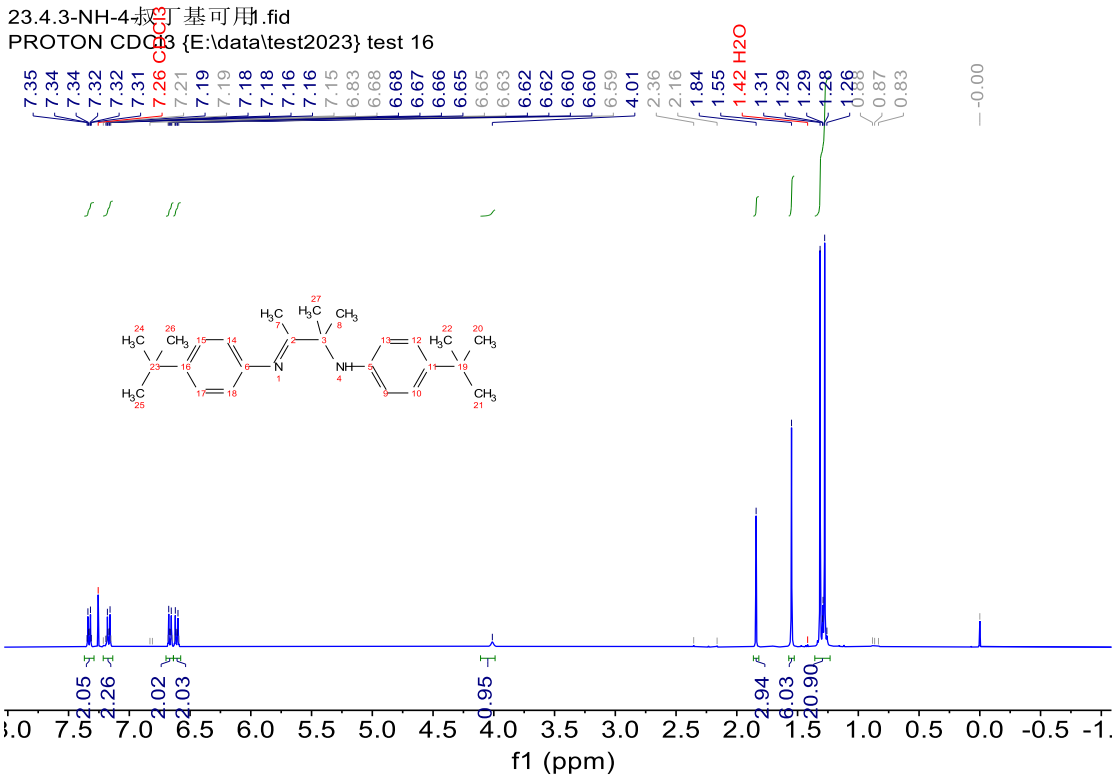

Figure S8. ^{1}H NMR spectrum of L7

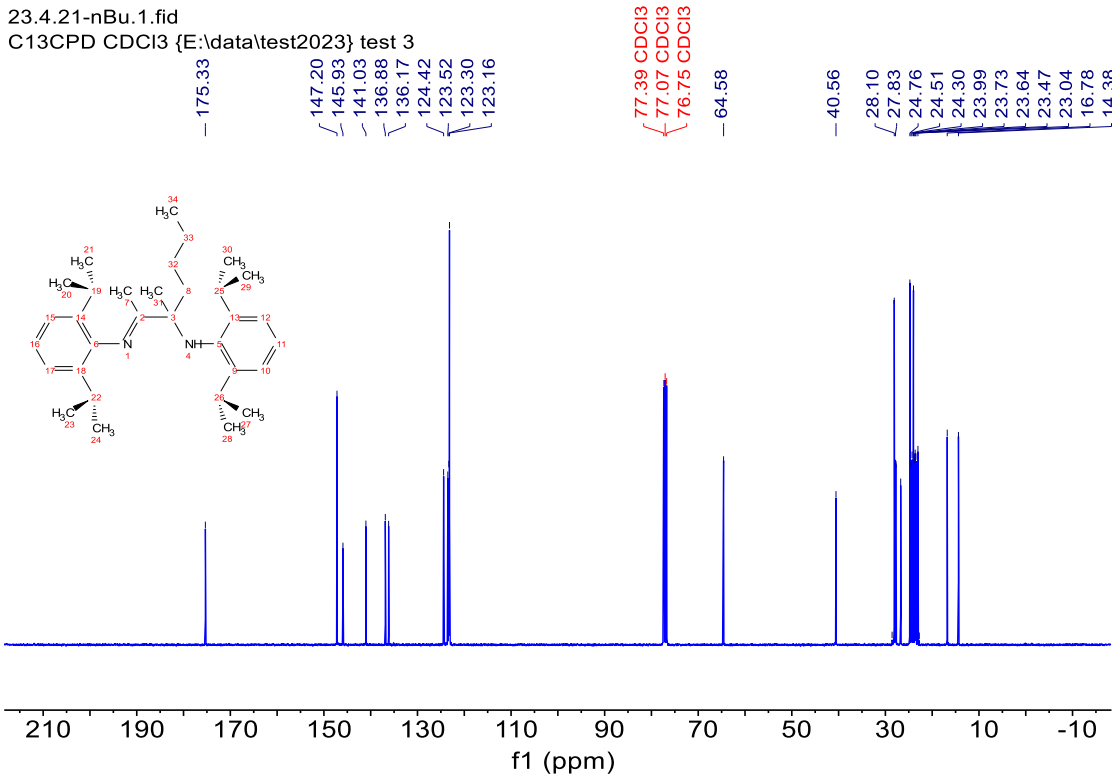

Figure S9. ^{13}C NMR spectrum of L1

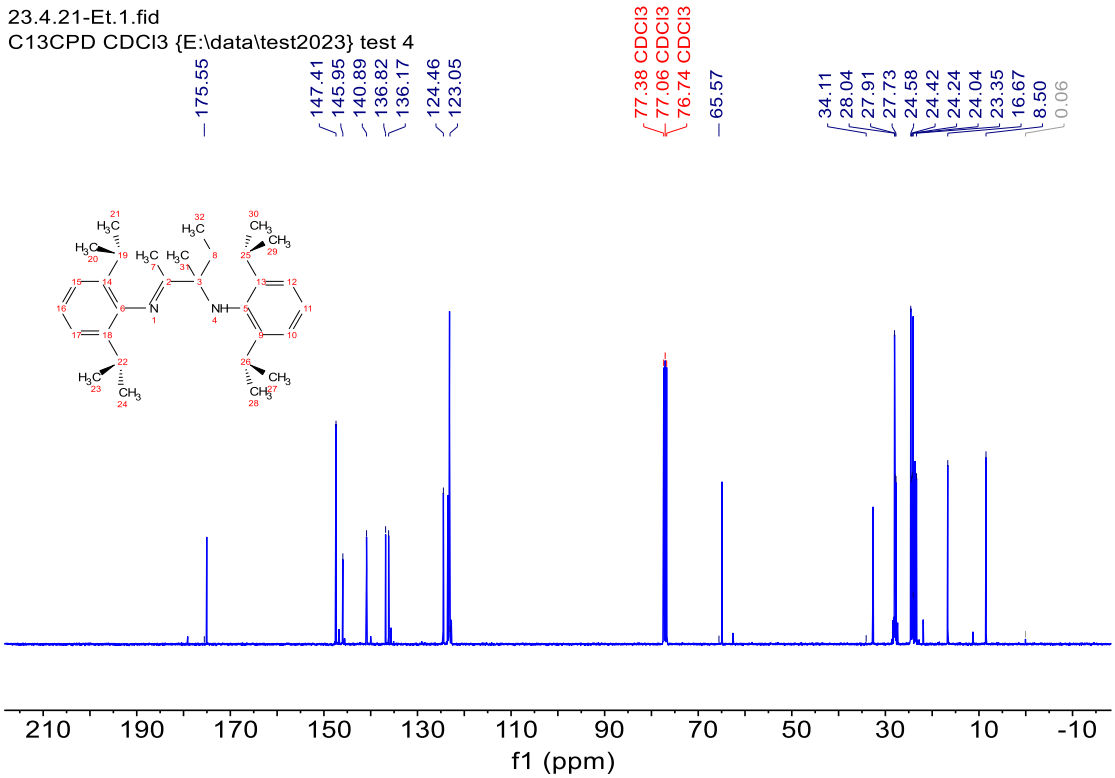

Figure S10. ^{13}C NMR spectrum of L2

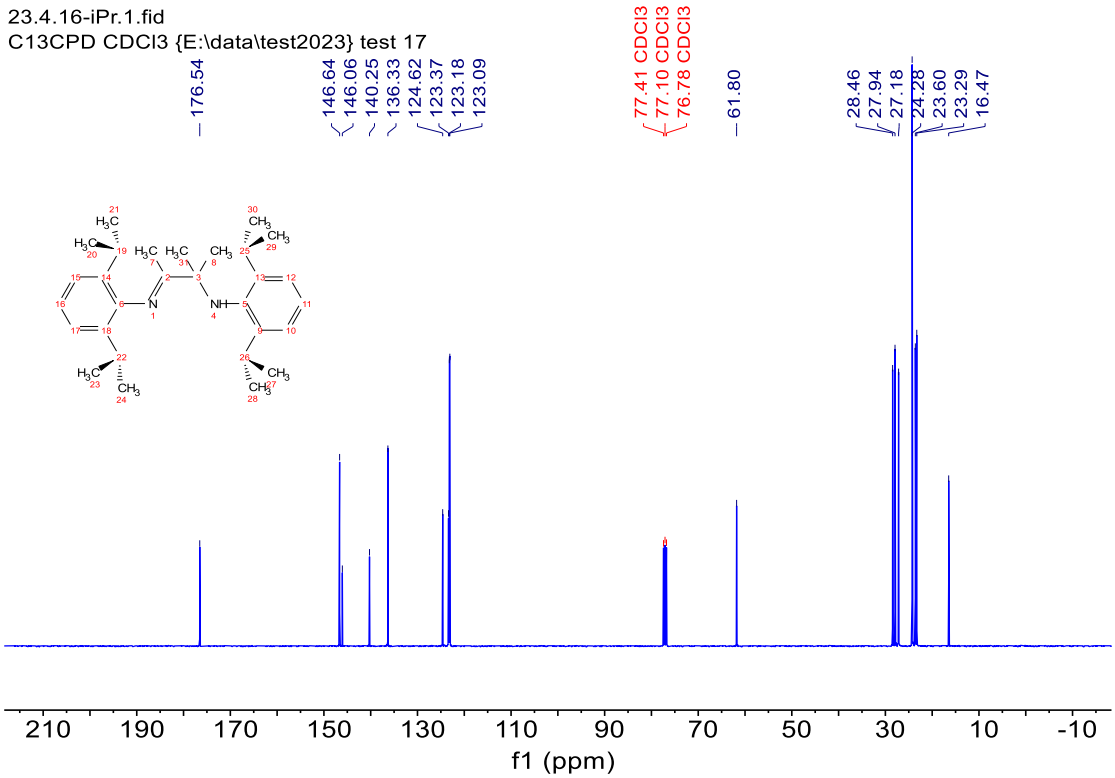

Figure S11. ^{13}C NMR spectrum of L3

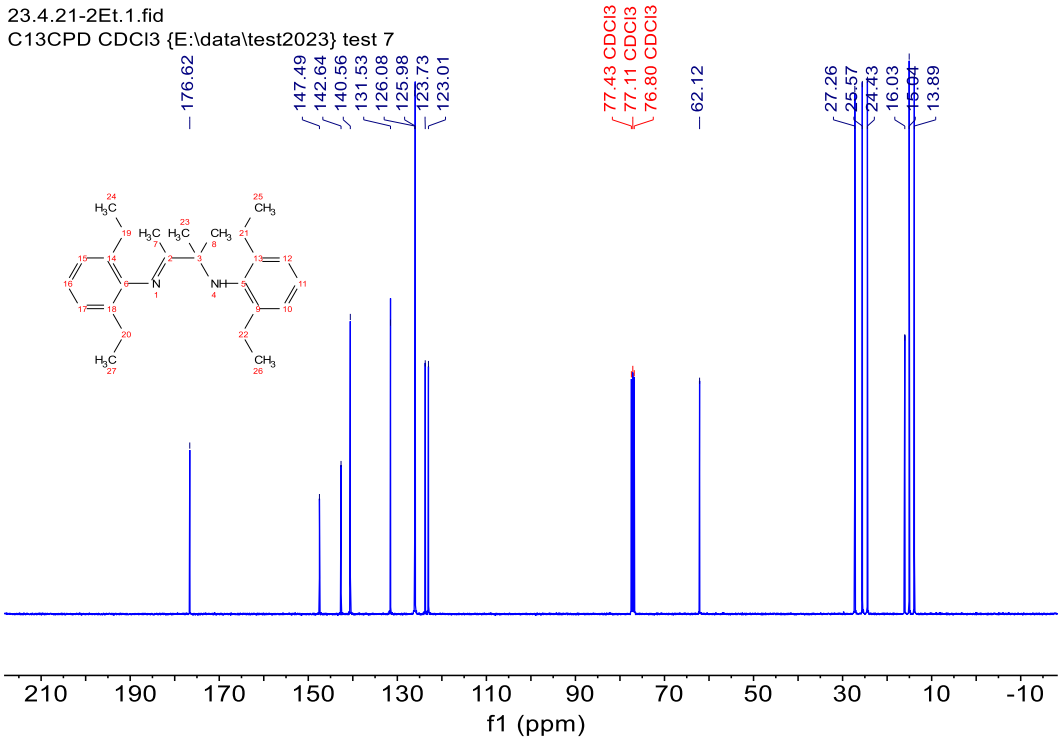

Figure S12. ^{13}C NMR spectrum of L4

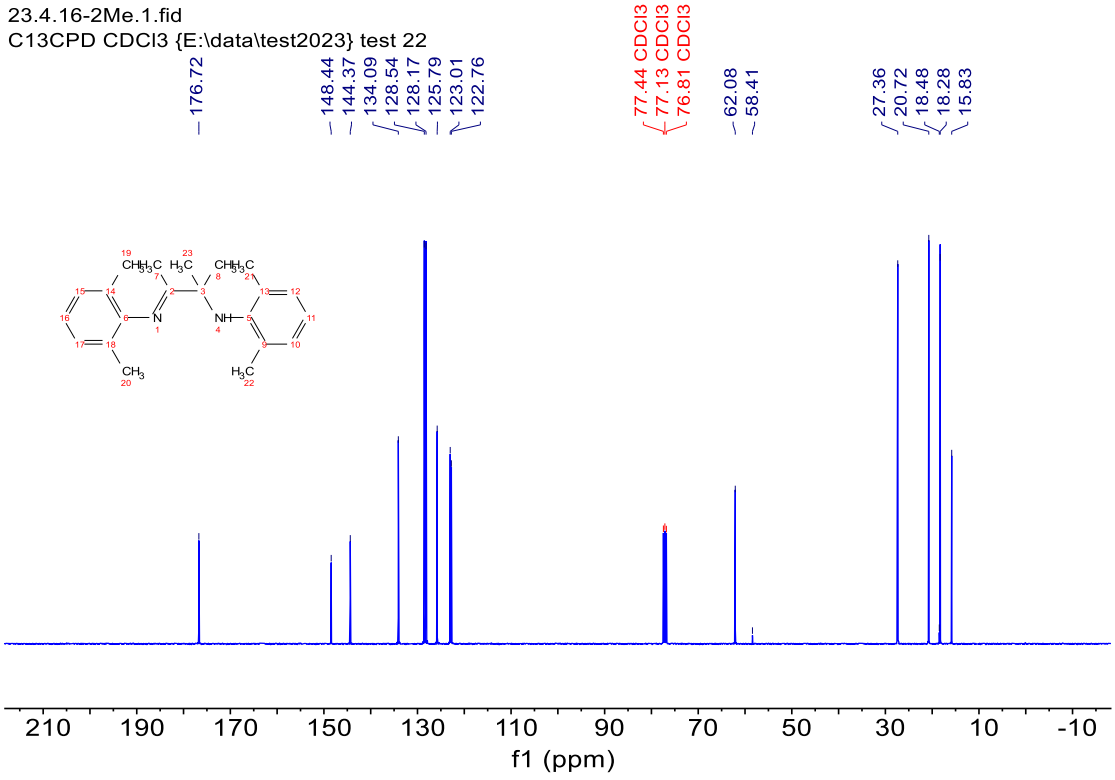

Figure S13. ^{13}C NMR spectrum of L5

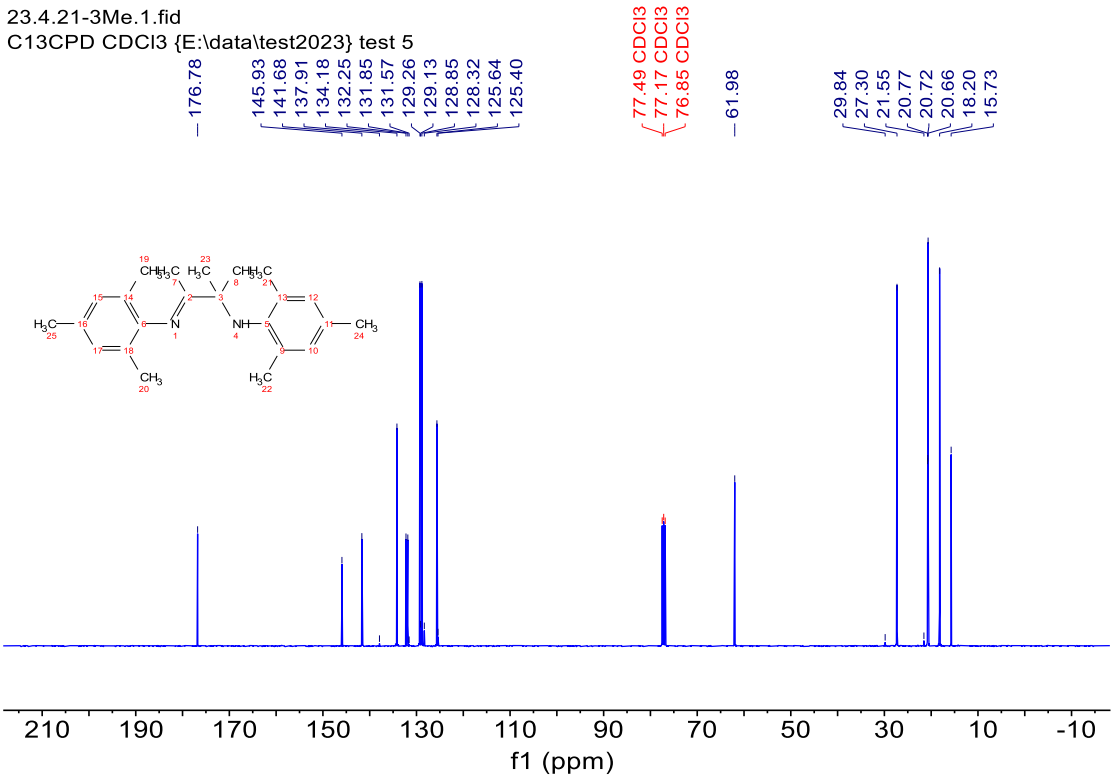

Figure S14. ^{13}C NMR spectrum of L6

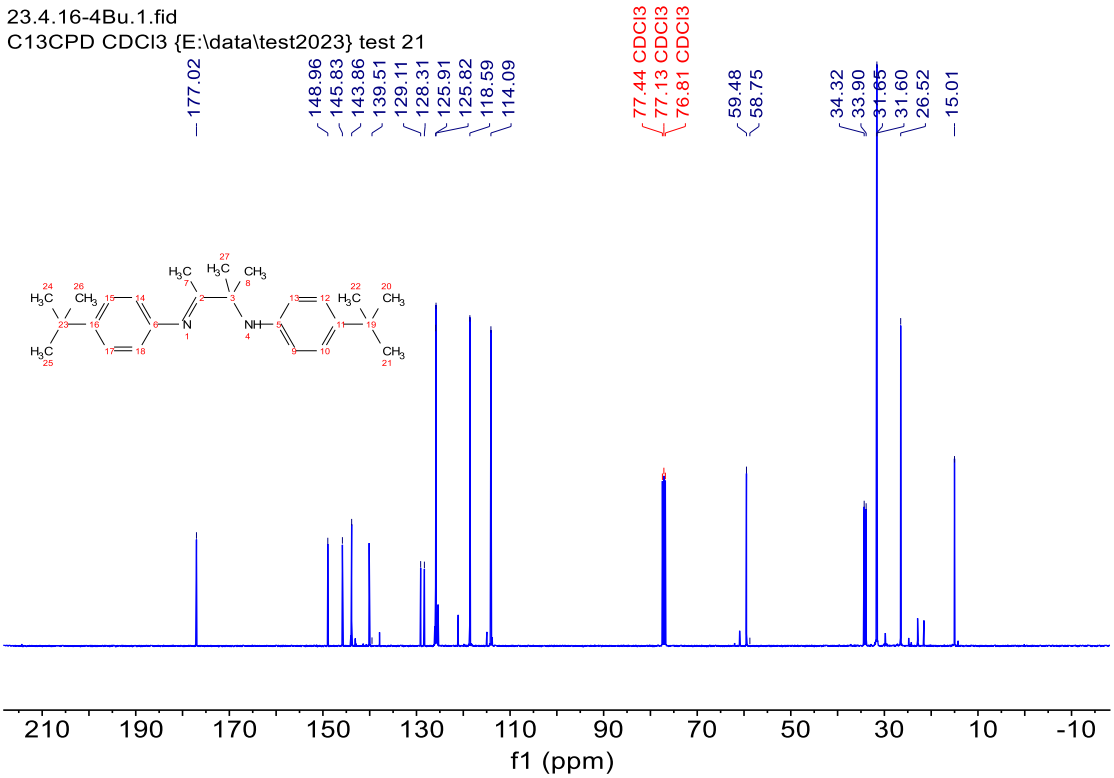

Figure S15. ^{13}C NMR spectrum of L7

The hydrogen atom treatment, restraints and constraints used in the refinement

Refinement of 2262742: The data were truncated by 0.84 angstrom due to the I/sigma drops below 2 at about 2theta = 50 (*ca.* 0.84 Å). No significant disorder found in this structure. The hydrogen atom (H2) on the nitrogen atom (N2) of amine group was located by difference Fourier syntheses and was refined freely. All of the other hydrogen atoms were placed at the calculated positions and were refined as riding model. The isotropic U value of hydrogen atoms (U_{iso}) were refined as: U_{iso}(N−H) = 1.2 U_{eq}(N), U_{iso}(C_{sp2}−H) = 1.2 U_{eq}(Csp2), U_{iso}(C_{sp3}−H) = 1.2 U_{eq}(C), and U_{iso}(CH_3) = 1.2 U_{eq}(C). The residual electron densities were of no chemical significance.

Refinement of 2262744: The data were truncated by 0.93 angstrom due to the I/sigma drops below 2 at about 2theta = 45 (*ca.* 0.93 Å). The linker fragment [$C(CH_3)C(CH_3)_2$, labeled as C13, C14, C15, C16, and C17) between two nitrogen atoms of the imine ligand were refined as two-components-disorder (C13~C17 and C13A~C17A) over two sites with occupancies 0.892:0.108, as well as the hydrogen atoms on the nitrogen atom of amine group. The methyl groups in one isopropyl of the two diisopropylphenyl (dipp) group were refined as two-components-disorder (C8~C9/C8A~C9A and C28~C29/C28A~C29A) over two sites with occupancies 0.542:0.458 and 0.412:0.588, respectively. The methylene and one chloride atom of the free solvent dichloromethane were refined as two-components-disorder (C30, Cl3 and C30A, Cl3A) over two sites with occupancies 0.646:0.354. The hydrogen atoms on the nitrogen atom of amine group cannot be located by difference Fourier syntheses due to disorder, and thus were placed at the calculated positions and were refined as riding model. The isotropic U value of hydrogen atoms (U_{iso}) were refined as: U_{iso}(N−H) = 1.2 U_{eq}(N), U_{iso}(C_{sp2}−H) = 1.2 U_{eq}(Csp2), U_{iso}(C_{sp3}−H) = 1.2 U_{eq}(C), and U_{iso}(CH_3) = 1.2 U_{eq}(C). Necessary restraints/constraints (SADI, DFIX, FLAT, RIGU and SIMU) were applied to prevent deformation of the disordered fragments and maintain its anisotropic displacement parameters within a reasonable range. The residual electron densities were of no chemical significance.

Refinement of 2262745: The whole structure was on mirror plane leading to a special disorder of the entire ligand across symmetry element wit occupancies of 0.5. The hydrogen atoms on the nitrogen atom of amine group cannot be located by difference Fourier syntheses due to disorder, and thus were placed at the calculated positions and were refined as riding model. The isotropic U value of hydrogen atoms (U_{iso}) were refined as: U_{iso}(N−H) = 1.2 U_{eq}(N), U_{iso}(C_{sp2}−H) = 1.2 U_{eq}(Csp2), U_{iso}(C_{sp3}−H) = 1.2 U_{eq}(C), and U_{iso}(CH_3) = 1.2 U_{eq}(C). Necessary restraints/constraints (DFIX, RIGU and SIMU) were applied to prevent deformation of the disordered fragments and maintain its anisotropic displacement parameters within a reasonable range. The residual electron densities were of no chemical significance.

Table S2. Crystal data and structure refinement for Co3 (CDCC 2262744).

Identification code	2262744
Empirical formula	$C_{30}H_{46}Cl_4CoN_2$
Formula weight	635.42
Temperature/K	300.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.271(4)
b/Å	19.167(9)
c/Å	21.451(10)
α/°	90
β/°	93.145(8)
γ/°	90
Volume/Å^3	3396(3)
Z	4
ρ_{calc}g/cm^3	1.243
μ/mm^{-1}	0.840
F(000)	1340.0
Crystal size/mm^3	0.26 × 0.23 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.852 to 45.814
Index ranges	$-8 \leq h \leq 8$, $-20 \leq k \leq 20$, $-23 \leq l \leq 22$
Reflections collected	18116
Independent reflections	4548 [R_{int} = 0.0683, R_{sigma} = 0.0605]
Data/restraints/parameters	4548/393/453
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0602, wR_2 = 0.1475
Final R indexes [all data]	R_1 = 0.0863, wR_2 = 0.1644
Largest diff. peak/hole / e Å^{-3}	0.49/-0.36

Table S3. Crystal data and structure refinement for Co4 (CDCC 2262745)

Identification code	2262745
Empirical formula	$C_{25}H_{36}Cl_2CoN_2$
Formula weight	494.39
Temperature/K	300.00
Crystal system	orthorhombic
Space group	Pnma
a/Å	14.7263(8)
b/Å	17.7923(12)
c/Å	9.6321(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2523.8(3)
Z	4
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	0.906
F(000)	1044.0
Crystal size/mm^3	0.29 × 0.26 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.822 to 59.99
Index ranges	$-20 \leq h \leq 18$, $-24 \leq k \leq 25$, $-13 \leq l \leq 13$
Reflections collected	72137
Independent reflections	3769 [R_{int} = 0.0852, R_{sigma} = 0.0342]
Data/restraints/parameters	3769/325/269
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.1037, wR_2 = 0.2471
Final R indexes [all data]	R_1 = 0.1283, wR_2 = 0.2585
Largest diff. peak/hole / e Å^{-3}	0.74/-0.58

Table S4. Crystal data and structure refinement for Co6 (CDCC 2262742).

Identification code	2262742
Empirical formula	$C_{23}H_{32}Cl_2CoN_2$
Formula weight	466.33
Temperature/K	300
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.3734(16)
b/Å	14.684(2)
c/Å	15.247(2)
α/°	90
β/°	108.415(2)
γ/°	90
Volume/Å^3	2416.0(6)
Z	4
ρ_{calc}g/cm^3	1.282
μ/mm^{-1}	0.942
F(000)	980.0
Crystal size/mm^3	0.26 × 0.23 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.932 to 50.082
Index ranges	$-13 \leq h \leq 12$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$
Reflections collected	16686
Independent reflections	4268 [R_{int} = 0.0585, R_{sigma} = 0.0559]
Data/restraints/parameters	4268/0/266
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0632, wR_2 = 0.1185
Final R indexes [all data]	R_1 = 0.0976, wR_2 = 0.1317
Largest diff. peak/hole / e Å^{-3}	0.69/-0.53